

CLAIMS

What is claimed is:

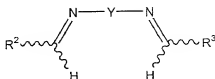
- 1 I. A method of synthesizing a diazaphosphacycle, comprising:
2 reacting a phosphine with a diimine and optionally one or more equivalents of an
3 acid halide, a sulfonyl halide, a phosphoryl halide, or an acid anhydride in the
4 substantial absence of O₂ to form the diazaphosphacycle, wherein the phosphine has
5 the formula I



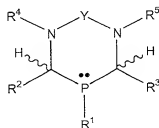
I

- 6 wherein,
7 R¹ is selected from the group consisting of substituted and unsubstituted aryl
8 groups, substituted and unsubstituted alkyl groups, substituted and unsubstituted
9 alkenyl groups, substituted and unsubstituted cycloalkyl groups, and substituted and
10 unsubstituted ferrocenyl groups.

- 1 2. The method of claim 1, wherein the diimine has the formula
2 II, and the diazaphosphacycle has the formula III,



II



III

- 3 wherein,
4 R² and R³ are independently selected from the group consisting of substituted and
5 unsubstituted aryl groups, substituted and unsubstituted alkyl groups, substituted
6 and unsubstituted cycloalkyl groups, substituted and unsubstituted heterocycl
7 groups, and substituted and unsubstituted ferrocenyl groups;

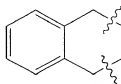
- 9 R^4 is selected from the group consisting of -H, substituted and unsubstituted alkyl
 10 groups, substituted and unsubstituted cycloalkyl groups, substituted and
 11 unsubstituted aryl groups, trialkylsilyl groups, triarylsilyl groups, alkyl diarylsilyl
 12 groups, dialkylarylsilyl groups, $-C(=O)-R^6$ groups, $-S(=O)_2-R^6$ groups,
 13 $-P(=O)R^6R^7$ groups, and $-C(=NR^6)-R^7$ groups;
- 14 R^5 is selected from the group consisting of -H, substituted and unsubstituted alkyl
 15 groups, substituted and unsubstituted cycloalkyl groups, substituted and
 16 unsubstituted aryl groups, trialkylsilyl groups, triarylsilyl groups, alkyl diarylsilyl
 17 groups, dialkylarylsilyl groups, $-C(=O)-R^7$ groups, $-S(=O)_2-R^6$ groups,
 18 $-P(=O)R^6R^7$ groups, and $-C(=NR^6)-R^7$ groups;
- 19 R^6 is selected from the group consisting of substituted and unsubstituted alkyl
 20 groups, substituted and unsubstituted alkenyl groups, substituted and unsubstituted
 21 cycloalkyl groups, substituted and unsubstituted aryl groups, -OH groups,
 22 substituted and unsubstituted alkoxy groups, substituted and unsubstituted aryloxy
 23 groups, -NH(alkyl) groups, -NH(aryl) groups, -N(aryl)₂ groups, -N(alkyl)₂ groups,
 24 -N(alkyl)(aryl) groups, -S-alkyl groups, and S-aryl groups;
- 25 R^7 is selected from the group consisting of substituted and unsubstituted alkyl
 26 groups, substituted and unsubstituted alkenyl groups, substituted and unsubstituted
 27 cycloalkyl groups, substituted and unsubstituted aryl groups, -OH groups,
 28 substituted and unsubstituted alkoxy groups, substituted and unsubstituted aryloxy
 29 groups, -NH(alkyl) groups, -NH(aryl) groups, -N(aryl)₂ groups, -N(alkyl)₂ groups,
 30 -N(alkyl)(aryl) groups, -S-alkyl groups, and S-aryl groups;
- 31 R^6 and R^7 may be part of the same alkyl group, alkenyl group, or aryl group such
 32 that R^4 and R^5 together with the two nitrogen atoms of the diazaphosphacycle form a
 33 ring; and
- 34 Y is a linking group selected from the group consisting of substituted and
 35 unsubstituted cycloalkyl groups, substituted and unsubstituted aryl groups,
 36 substituted and unsubstituted alkenyl groups, silyl groups, substituted alkyl groups,

- 37 and groups having the formula $-(CH_2)_n-$ wherein n is selected from the group
38 consisting of 0, 1, 2, and 3.

1 3. The method of claim 2, wherein n is 0.

1 4. The method of claim 2, wherein Y is a cycloalkyl group,
2 wherein one of the N atoms of the diimine is bonded to a first ring member C atom
3 of the cycloalkyl group and the other N atom of the diimine is bonded to a second
4 ring member C atom that is bonded to the first ring member C atom.

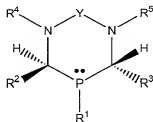
1 5. The method of claim 2, wherein Y has the formula



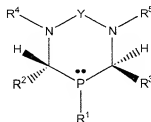
2
3 and the benzene ring of Y may be additionally substituted.

1 6. The method of claim 2, wherein R^2 and R^3 are identical but
2 are not part of the same group.

1 7. The method of claim 2, wherein the diazaphosphacycle is
2 selected from the group consisting of compounds of formula IIIA, compounds of
3 formula IIIB, and mixtures thereof,



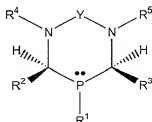
4 IIIA



IIIB

1 8. The method of claim 7, wherein n is 0.

- 1 9. The method of claim 2, wherein the diazaphosphacycle has
2 the formula IIIC,



IIIC

- 1 10. The method of claim 9, wherein n is 0.
- 1 11. The method of claim 1, wherein the phosphine and the
2 diimine are reacted in the presence of an acid.
- 1 12. The method of claim 2, wherein the phosphine and the
2 diimine are reacted in the presence of the acid halide, the sulfonyl halide, the
3 phosphoryl halide, or the acid anhydride, and at least one of R⁴ and R⁵ is not H.
- 1 13. The method of claim 2, wherein the phosphine and the
2 diimine are reacted in the presence of the acid halide, and further wherein R⁴ is a
3 -C(=O)-R⁶ group and R⁵ is a -C(=O)-R⁷ group.
- 1 14. The method of claim 1, wherein the phosphine and the
2 diimine are reacted in the presence of phthaloyl dichloride or phthaloyl dibromide.
- 1 15. The method of claim 1, wherein R¹ comprises one or more
2 -PH₂ group such that the phosphine is a polyphosphine.
- 1 16. The method of claim 15, wherein the polyphosphine is
2 selected from the group consisting of 1,2-diphosphinoethane,
3 1,2-diphosphinoethylene, 1,3-diphosphinopropane, substituted and unsubstituted
4 1,2-diphosphinobenzene groups, substituted and unsubstituted

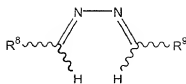
5 1,8-diphosphinoanthracene groups, substituted and unsubstituted 1,8-diphosphino-
6 9,10-dihydroanthracene groups, substituted and unsubstituted
7 1,8-diphosphinoxanthene groups, and substituted and unsubstituted
8 1,1'-diphosphinoferrocene groups.

1 17. The method of claim 1, wherein the phosphine, the diimine,
2 and optionally the acid halide are reacted in a substantially deoxygenated solvent
3 comprising an ether, an alcohol, water, dichloroethane, or combinations thereof.

1 18. The method of claim 2, wherein a library of different
2 diazaphosphacycles is produced using a combinatorial method.

1 19. The method of claim 1, further comprising reacting an acid
2 halide, an acid anhydride, a phosphoryl halide, or a sulfonyl halide with the
3 diazaphosphacycle to produce a second diazaphosphacycle wherein R^4 and R^5 are
4 both -H in the diazaphosphacycle and at least one of R^4 and R^5 is not -H in the
5 second diazaphosphacycle.

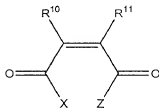
1 20. A method of synthesizing a diazaphosphacycle, comprising:
2 (a) reacting a diimine with an acid halide, a diacid
3 dihalide, a sulfonyl halide, a disulfonyl dihalide, a
4 phosphoryl halide, or a diphosphoryl dihalide to form
5 a dihalo intermediate compound; and
6 (b) reacting the dihalo intermediate compound with a
7 phosphine of formula R^1-PH_2 in the substantial absence
8 of O_2 to form the diazaphosphacycle,
9 wherein R^1 is selected from the group consisting of substituted and unsubstituted
10 aryl groups, substituted and unsubstituted alkyl groups, substituted and
11 unsubstituted alkenyl groups, substituted and unsubstituted cycloalkyl groups, and
12 substituted and unsubstituted ferrocenyl groups; and
13 the diimine has the formula IV



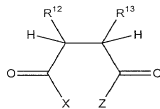
IV

14 wherein R^8 and R^9 are independently selected from the group consisting of
 15 substituted and unsubstituted aryl groups, substituted and unsubstituted alkyl
 16 groups, substituted and unsubstituted cycloalkyl groups, substituted and
 17 unsubstituted heterocyclyl groups, and substituted and unsubstituted ferrocenyl
 18 groups.

1 21. The method of claim 20, wherein the diimine is reacted with a
 2 diacyl dihalide, and the diacyl dihalide has the formula V or the formula VI

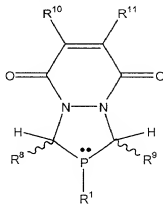


V

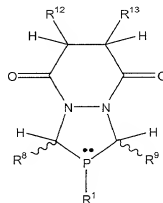


VI

3 and the diazaphosphacycle has the formula VII or the formula VIII



VII



VIII

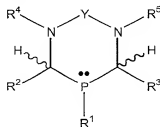
5
 6 wherein,

- 7 R^{10} , R^{11} , R^{12} , and R^{13} are independently selected from the group consisting of -H,
 8 substituted and unsubstituted alkyl groups, substituted and unsubstituted cycloalkyl
 9 groups, and substituted and unsubstituted aryl groups;
 10 R^{10} and R^{11} may join together to form a substituted or unsubstituted aryl group or a
 11 substituted or unsubstituted cycloalkenyl group;
 12 R^{12} and R^{13} may join together to form a substituted or unsubstituted cycloalkenyl
 13 group or a substituted or unsubstituted cycloalkyl group; and
 14 X and Z are independently selected from -Cl or -Br.

1 22. The method of claim 21, wherein R^8 and R^9 are identical but
 2 are not part of the same group and R^8 and R^9 are substituted or unsubstituted aryl
 3 groups.

1 23. The method of claim 21, wherein the diacyl dihalide is
 2 phthaloyl dichloride.

1 24. A diazaphosphacycle, comprising a compound having the
 2 formula III and salts of the compound



III

3
 4 wherein

- 5 R^1 is selected from the group consisting of substituted and unsubstituted aryl
 6 groups, substituted and unsubstituted alkyl groups, substituted and unsubstituted
 7 alkenyl groups, substituted and unsubstituted cycloalkyl groups, and substituted and
 8 unsubstituted ferrocenyl groups;
 9 R^2 and R^3 are independently selected from the group consisting of substituted and
 10 unsubstituted aryl groups, substituted and unsubstituted alkyl groups, substituted

- 11 and unsubstituted cycloalkyl groups, substituted and unsubstituted heterocyclyl
12 groups, and substituted and unsubstituted ferrocenyl groups;
- 13 R^4 is selected from the group consisting of -H, substituted and unsubstituted alkyl
14 groups, substituted and unsubstituted cycloalkyl groups, substituted and
15 unsubstituted aryl groups, trialkylsilyl groups, triarylsilyl groups, alkyl diarylsilyl
16 groups, dialkylarylsilyl groups, $-C(=O)-R^6$ groups, $-S(=O)_2-R^6$ groups,
17 $-P(=O)R^6R^7$ groups, and $-C(=NR^6)-R^7$ groups;
- 18 R^5 is selected from the group consisting of -H, substituted and unsubstituted alkyl
19 groups, substituted and unsubstituted cycloalkyl groups, substituted and
20 unsubstituted aryl groups, trialkylsilyl groups, triarylsilyl groups, alkyl diarylsilyl
21 groups, dialkylarylsilyl groups, $-C(=O)-R^7$ groups, $-S(=O)_2-R^6$ groups,
22 $-P(=O)R^6R^7$ groups, and $-C(=NR^6)-R^7$ groups;
- 23 R^6 is selected from the group consisting of substituted and unsubstituted alkyl
24 groups, substituted and unsubstituted alkenyl groups, substituted and unsubstituted
25 cycloalkyl groups, substituted and unsubstituted aryl groups, -OH groups,
26 substituted and unsubstituted alkoxy groups, substituted and unsubstituted aryloxy
27 groups, -NH(alkyl) groups, -NH(aryl) groups, -N(aryl)₂ groups, -N(alkyl)₂ groups,
28 -N(alkyl)(aryl) groups, -S-alkyl groups, and S-aryl groups;
- 29 R^7 is selected from the group consisting of substituted and unsubstituted alkyl
30 groups, substituted and unsubstituted alkenyl groups, substituted and unsubstituted
31 cycloalkyl groups, substituted and unsubstituted aryl groups, -OH groups,
32 substituted and unsubstituted alkoxy groups, substituted and unsubstituted aryloxy
33 groups, -NH(alkyl) groups, -NH(aryl) groups, -N(aryl)₂ groups, -N(alkyl)₂ groups,
34 -N(alkyl)(aryl) groups, -S-alkyl groups, and S-aryl groups;
- 35 R^6 and R^7 may be part of the same alkyl group, alkenyl group, or aryl group such
36 that R^4 and R^5 together with the two nitrogen atoms of the diazaphosphacycle form a
37 ring; and

38 Y is a linking group selected from the group consisting of substituted and
39 unsubstituted cycloalkyl groups, substituted and unsubstituted aryl groups,
40 substituted and unsubstituted alkenyl groups, silyl groups, substituted alkyl groups,
41 and groups having the formula $-(CH_2)_n-$ wherein n is selected from the group
42 consisting of 0, 1, 2, and 3.

1 25. A transition metal complex, comprising the
2 diazaphosphacycle of claim 24 and a transition metal, wherein the phosphorus atom
3 of the diazaphosphacycle is bonded to the transition metal.

1 26. The transition metal complex of claim 25, wherein the
2 transition metal is selected from the group consisting of Rh, Ru, Pd, Pt, Ir, Ni, Co,
3 and Fe.

1 27. The transition metal complex of claim 25, wherein the
2 transition metal complex has catalytic activity.

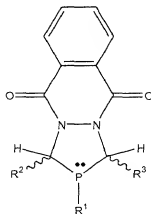
1 28. A method of catalyzing a chemical reaction, comprising using
2 the transition metal complex of claim 27 as a catalyst.

1 29. The diazaphosphacycle of claim 24, wherein n is 0.

1 30. The diazaphosphacycle of claim 29, wherein R^4 and R^5 are
2 both -H.

1 31. The diazaphosphacycle of claim 29, wherein R^4 is a
2 $-C(=O)-R^6$ group and R^5 is a $-C(=O)-R^7$ group.

- 1 32. The diazaphosphacycle of claim 31, wherein, the
2 diazaphosphacycle has the formula IX



IX

- 3
4 wherein the aromatic benzene ring in the compound of formula IX may be
5 substituted or unsubstituted.

- 1 33. A transition metal complex, comprising the
2 diazaphosphacycle of claim 31 and a transition metal, wherein the phosphorus atom
3 of the diazaphosphacycle is bonded to the transition metal.

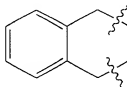
- 1 34. The transition metal complex of claim 33, wherein the
2 transition metal is selected from the group consisting of Rh, Ru, Pd, Pt, Ir, Ni, Co,
3 and Fe.

- 1 35. The transition metal complex of claim 33, wherein the
2 transition metal complex has catalytic activity.

- 1 36. A method of catalyzing a chemical reaction, comprising using
2 the transition metal complex of claim 35 as a catalyst.

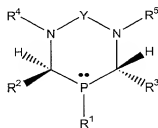
- 1 37. The diazaphosphacycle of claim 24, Y is a cycloalkyl group,
2 wherein one of the N atoms is bonded to a first ring member C atom of the
3 cycloalkyl group and the other N atom is bonded to a second ring member C atom
4 that is bonded to the first ring member C atom.

- 1 38. The diazaphosphacycle of claim 24, wherein Y has the
2 formula

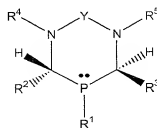


- 3
4 and the benzene ring of Y may be additionally substituted.

- 1 39. The diazaphosphacycle of claim 24, wherein the
2 diazaphosphacycle has the formula IIIA, the formula IIIB, or is a mixture thereof



3 IIIA



IIIB

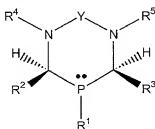
- 1 40. A transition metal complex, comprising the
2 diazaphosphacycle of claim 39 and a transition metal, wherein the phosphorus atom
3 of the diazaphosphacycle is bonded to the transition metal.

- 1 41. The transition metal complex of claim 40, wherein the
2 transition metal is selected from the group consisting of Rh, Ru, Pd, Pt, Ir, Ni, Co,
3 and Fe.

- 1 42. The transition metal complex of claim 40, wherein the
2 transition metal complex has catalytic activity.

- 1 43. A method of catalyzing a chemical reaction, comprising using
2 the transition metal complex of claim 42 as a catalyst.

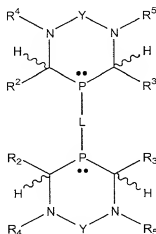
- 1 44. The diazaphosphacycle of claim 24, wherein the
2 diazaphosphacycle has the formula IIIC



- 3 IIIC

- 1 45. The diazaphosphacycle of claim 24, wherein the
2 diazaphosphacycle is present as a mixture of enantiomers.

- 1 46. The diazaphosphacycle of claim 24, wherein the
2 diazaphosphacycle has the formula X



- 3 X
- 4 wherein L is a linking group selected from the group consisting of substituted and
5 unsubstituted alkyl groups, substituted and unsubstituted alkenyl groups, substituted
6 and unsubstituted aryl groups, and substituted and unsubstituted ferrocenyl groups.

1 47. The diazaphosphacycle of claim 46, wherein L is selected
2 from the group consisting of ethane, ethylene, propane, benzene, anthracene, 9,10-
3 dihydroanthracene, xanthene, and ferrocene.

1 48. A transition metal complex, comprising the
2 diazaphosphacycle of claim 46 and a transition metal, wherein at least one of the
3 phosphorus atoms of the diazaphosphacycle is bonded to the transition metal.

1 49. The transition metal complex of claim 48, wherein the
2 transition metal is selected from the group consisting of Rh, Ru, Pd, Pt, Ir, Ni, Co,
3 and Fe.

1 50. The transition metal complex of claim 48, wherein two of the
2 phosphorus atoms of the diazaphosphacycle are bonded to the transition metal.

1 51. A combinatorial library of diazaphosphacycles, comprising a
2 collection of different diazaphosphacycles according to claim 24.

1 52. A combinatorial library of transition metal complexes,
2 comprising a collection of different transition metal complexes according to claim
3 25.

1 53. A method of synthesizing a diazaphosphacycle transition
2 metal complex, comprising reacting the diazaphosphacycle of claim 24 with a
3 starting transition metal complex to produce the diazaphosphacycle transition metal
4 complex, wherein the starting transition metal complex includes at least one ligand
5 that is replaced by the diazaphosphacycle.

1 54. The method of claim 53, wherein the ligand replaced by the
2 diazaphosphacycle is selected from the group consisting of phosphines; amines;
3 diamines; CO; Cl; Br; nitriles; 1,5-cyclooctadiene, norbornadiene, and other
4 dienes; alkenes; arenes; ketones; alcohols; ethers; thiols; and sulfoxides.